Notes

Chemistry of 3-Methoxy-3-methyl-2-oxa-7,7-dichloronorcaranes, the Dichlorocarbene Adducts of 2-Methoxy-2-methyl-3,4-dihydro-2*H*-pyrans[1]

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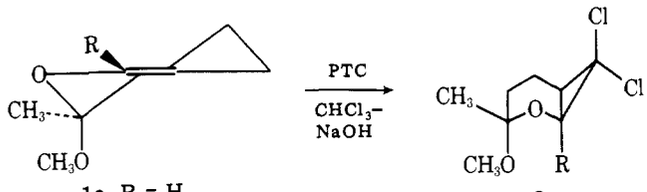
We wish to describe an improved procedure for the synthesis of 3-alkoxy-2-oxa-7,7-dichloronorcaranes, employing phase-transfer catalysis (PTC),[3] and the chemistry of these dichlorocarbene adducts of 2-alkoxy-3,4-dihydro-2*H*-pyrans that results in the convenient preparation of potentially useful synthons of defined stereochemistry. For this study, 3-methoxy-3-methyl-2-oxa-7,7-dichloronorcarane (**2a**) and 3-methoxy-1,3-dimethyl-2-oxa-7,7-dichloronorcarane (**2b**) were prepared from the corresponding 2-methoxy-2-methyl- (**1a**)[4]



1a, R = H
1b, R = CH_3

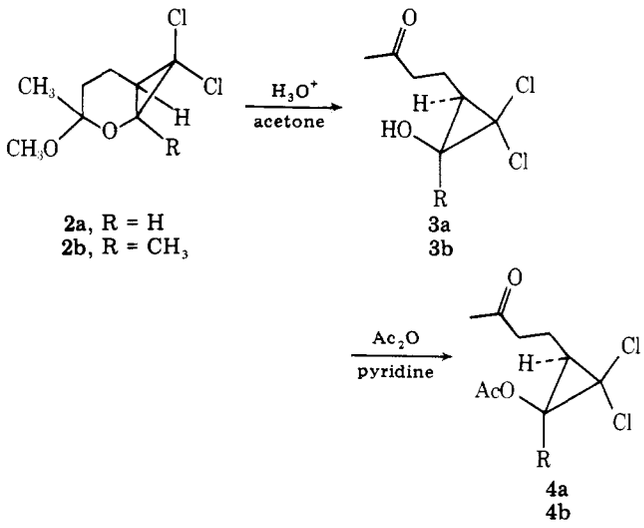
2a
2b

and 2-methoxy-2,6-dimethyl-3,4-dihydro-2*H*-pyran (**1b**)[4] in a two-phase chloroform–sodium hydroxide mixture using cetyltrimethylammonium chloride as the phase-transfer catalyst. For the efficient and convenient synthesis of these rather labile compounds,[5] this method is an improvement over our previously described procedure of generating the dichlorocarbene by the decomposition of ethyl trichloroacetate with sodium methoxide.[6]

NMR and GLC analyses of the crude and purified product indicated that only one stereoisomer is formed when adding the dichlorocarbene generated from PTC to these two 2-methyl substituted 3,4-dihydro-2*H*-pyrans **1a** and **1b**.[7] The adducts **2a** and **2b** have been tentatively assigned the trans configuration where the dichlorocarbene has added trans to the methoxy group.[8] This assignment is based entirely on the chemical shift of the C-1 proton [δ 3.56 (d, J = 8 Hz)] of **2a** as compared to the same proton in *trans*-3-methoxy-2-oxa-7,7-dichloronorcarane [δ 3.50 (d, J = 8 Hz)] and *cis*-3-methoxy-2-oxa-7,7-dichloronorcarane [δ 3.71 (d, J = 8 Hz)].[6]

Acid hydrolysis (trace of 1 N H_2SO_4 in acetone) of the 3-methoxy-2-oxa-7,7-dichloronorcares **2a** and **2b** afforded *cis*-2,2-dichloro-3-(3-ketobutyl)cyclopropanol (**3a**) and *cis*-2,2-dichloro-3-(3-ketobutyl)-1-methylcyclopropanol (**3b**), respectively. The cyclopropanols were isolated and characterized as the corresponding acetates **4a** and **4b**.[9,10]

The expected cis stereochemistry of the cyclopropanols was confirmed in the case of **3a** by NMR analysis of both the cyclopropanol **3a** and its acetate **4a**. The coupling constants of the doublet for the C-1 proton at δ 3.67 for **3a** and at δ 4.30 for **4a** are 7.5 and 8.0 Hz, respectively. Comparing the magnitude of this vicinal coupling with two model compounds, *cis*- and *trans*-1,1-dichloro-2-ethoxy-3-methylcyclopropane, where the coupling constants are 8.5 and 4.8 Hz,[11] respectively, for the C-2 proton doublet at δ 3.36 for the cis isomer and at δ 2.98



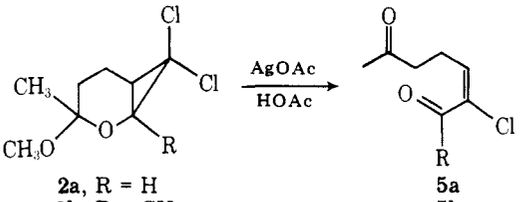
2a, R = H
2b, R = CH_3

3a
3b

4a
4b

for the trans isomer clearly demonstrates the stereochemistry of the cyclopropanol **3a** to be cis.

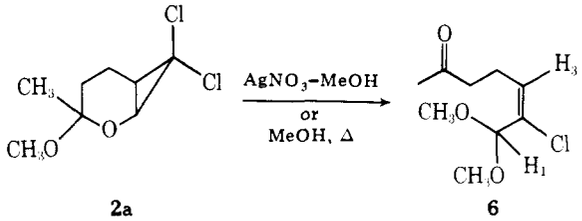
Solvolysis of the 2-oxa-7,7-dichloronorcaranes **2a** and **2b** in silver acetate–acetic acid yielded (*E*)-2-chloro-6-keto-2-heptenal (**5a**) and (*E*)-3-chloro-3-octene-2,7-dione (**5b**), respectively.



2a, R = H
2b, R = CH_3

5a
5b

In contrast, solvolysis of **2a** in silver nitrate–methanol or in refluxing methanol after 6 hours afforded (*E*)-2-chloro-6-keto-2-heptenal dimethyl acetal (**6**), which could be hydrolyzed in dilute acid (trace of 1 N H_2SO_4 in acetone for 30 min) to the heptenal **5a**. Spin decoupling experiments with **6** established that the coupling constant for the allylic coupling was very small ($J_{1,3}$ < 1.0 Hz)[12] and consequently confirmed the double-bond stereochemistry as *E*.



2a

6

Solvolysis of **2b** in silver nitrate–methanol resulted in a mixture of (*E*)-3-chloro-3-octene-2,7-dione (**5b**) and a monoketal. Treatment with dilute acid (trace of 1 N H_2SO_4 in acetone for 30 min) converted the mixture to the dione **5b**. (*E*)-3-Chloro-3-octene-2,7-dione (**5b**) could also be obtained after refluxing **2b** in methanol for 2 h.

For all of the ring-opened products **5–6** from these solvolysis reactions of the 3-methoxy-2-oxa-7,7-dichloronorcaranes, the *E* stereochemistry of the double bond is expected. Solvolysis of the syn chlorine substituent[13] results in a concerted disrotatory ring opening of the dichlorocarbene adduct **2**, gener-

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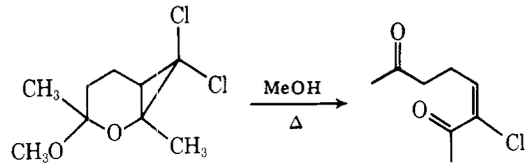
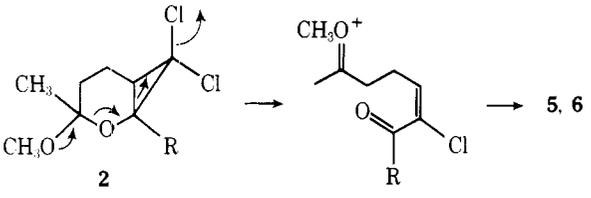


2b 5b

ating the *E* double bond.[14] These products, as well as the cyclopropanols, should prove useful in synthesis because of their functionality and stereochemistry, and ease of preparation.



Experimental Section[15]

General Comments. The preparation of 2-methoxy-2-methyl- (**1a**) and 2-methoxy-2,6-dimethyl-3,4-dihydro-2*H*-pyran (**1b**) has been described.[4] Gas chromatographic analyses (GLC) were performed on 200 × 0.3 cm (i.d.) glass columns packed with 3.8% silicon gum rubber SE-30 (methyl) or 10% silicon gum rubber XE-60 (25% cyanoethyl, methyl) supported on 60–80 mesh Chromosorb W (AW, DMCS). Column chromatography was performed on 60–100 mesh Floridin magnesium silicate (Florisil) columns by eluting with pentane–Et_2O. Distillations were accomplished with a short-path or Kugelrohr apparatus; all boiling points are uncorrected. The assigned structure of each product was consistent with the spectral data. Composition analyses (±0.4% for C, H, Cl) for all new compounds were submitted to the editor. Representative experiments are described to illustrate these reactions, and significant data on all new compounds are included in the Experimental Section.

3-Methoxy-3-methyl-2-oxa-7,7-dichloronorcarane (2a). To a stirred and warmed (50 °C) mixture of 2.56 g (20 mmol) of 2-methoxy-2-methyl-3,4-dihydro-2*H*-pyran (**1a**) and 10 mg (33 μmol) of cetyltrimethylammonium chloride in 6 mL of chloroform was added slowly (15 min) a solution of 6.4 g of NaOH in 13 mL of H_2O. After 2 h at 50 °C, the mixture was cooled and partitioned between water and Et_2O. The organic phase was separated, washed with water until the washings were neutral (Litmus test), and dried ($MgSO_4$). Removal of solvent in vacuo afforded 3.98 g of a 3:1 (GLC) mixture of **2a** and **5a**. Column chromatography afforded 2.90 g (69%) of 3-methoxy-3-methyl-2-oxa-7,7-dichloronorcarane (**2a**): bp 100 °C (12 torr); NMR ($CDCl_3$) δ 3.56 (1 H, d, J = 8 Hz), 3.27 (3 H, s), 2.36–1.42 (5 H, m), 1.28 (3 H, s); MS *m/e* (relative intensity) 183 (11), 181 (26), 179 (13), 177 (4), 175 (17), 149 (8), 147 (30), 113 (2), 111 (22), 109 (35), 85 (29), 72 (33), 43 (100).

3-Methoxy-1,3-dimethyl-2-oxa-7,7-dichloronorcarane (2b): bp 110 °C (8 torr); NMR (CCl_4) δ 3.23 (3 H, s), 1.53 (3 H, s) superimposed on 2.55–1.27 (5 H, m), 1.21 (3 H, s); MS *m/e* (relative intensity) 226 (M^+, 0.75), 224 (M^+, 1), 209 (1), 197 (0.75), 195 (3), 193 (5), 191 (1), 189 (4), 185 (1), 183 (7), 181 (10), 159 (2), 157 (6), 113 (4), 111 (11), 109 (17), 85 (18), 43 (100).

***cis*-2,2-Dichloro-3-(3-ketobutyl)cyclopropanol Acetate (4a).** To a solution of 1.00 g (48 mmol) of 3-methoxy-3-methyl-2-oxa-7,7-dichloronorcarane (**2a**) in 10 mL of acetone was added 0.1 mL of a 1 N H_2SO_4 solution. After stirring for 30 min, the mixture was poured into a saturated $NaHCO_3$ solution and extracted with Et_2O. The organic phase was washed with brine and dried ($MgSO_4$), and the solvent was removed in vacuo, affording 840 mg (93%) of *cis*-2,2-dichloro-3-(3-ketobutyl)cyclopropanol (**3a**).[16]

After a solution of the crude cyclopropanol **3a** in 6 mL of Ac_2O–pyridine (1:1) had stirred for 17 h, 3.2 mL of MeOH was added. After 30 min, the mixture was partitioned between Et_2O and cold water. The separated organic layer was then washed twice with cold 1 N H_2SO_4, twice with brine, once with saturated $NaHCO_3$, and again with brine. After drying ($MgSO_4$) and removing the solvent in vacuo, the crude acetate (985 mg) was purified by column chromatography, yielding 780 mg (67%) of *cis*-2,2-dichloro-3-(3-ketobutyl)cyclopropanol acetate (**4a**): IR (film) 1760, 1718 cm^{-1}; NMR ($CDCl_3$) δ 4.30 (1 H, d, J = 8.0 Hz), 2.61 (2 H, t, J = 7 Hz), 2.14 (3 H, s), 2.10 (3 H, s), 1.88–1.56 (3 H, m); MS *m/e* (relative intensity) 242 (M^+, 0.5), 240 (M^+, 2.5), 238 (M^+, 3.6), 199 (4), 197 (12), 195 (16), 183 (2), 181 (8), 179 (12), 163 (11), 161 (33), 145 (5), 143 (12), 43 (100).

***cis*-2,2-Dichloro-3-(3-ketobutyl)-1-methylcyclopropanol Acetate (4b).** Following the procedure above, hydrolysis of **2b** afforded **3b**[17] that on acetylation yielded a mixture, which was separated and isolated by column chromatography, of **4b** (30%) and **5b** (60%). *cis*-2,2-Dichloro-3-(3-ketobutyl)-1-methylcyclopropanol acetate (**4b**): IR (film) 1760, 1717 cm^{-1}; NMR (CCl_4) δ 2.56 (2 H, t, J = 7 Hz), 2.10 (3 H, s), 2.04 (3 H, s), 1.71 (3 H, s) superimposed on 1.82–1.18 (3 H, m).

(*E*)-2-Chloro-6-keto-2-heptenal (5a). After refluxing a solution of 259 mg (1.23 mmol) of 3-methoxy-3-methyl-2-oxa-7,7-dichloronorcarane (**2a**) and 250 mg (1.48 mmol) of silver acetate in 5 mL of HOAc for 2 h, 2 mL of H_2O was added and the heating continued for 15 min longer. After cooling, the reaction mixture was extracted with CH_2Cl_2. The organic phase was washed with brine, saturated $NaHCO_3$, and brine again and dried ($MgSO_4$), and then the solvent was removed in vacuo. Column chromatography afforded 135 mg (68%) of (*E*)-2-chloro-6-keto-2-heptenal (**5a**) as a colorless oil: IR (film) 1715, 1700, 1625 cm^{-1}; UV_{max} (isopropyl alcohol) 236, 286 sh nm (ε 12 000, 560); NMR (CCl_4) δ 9.25 (1 H, s), 6.88 (1 H, t with further fine splitting, J = 7 Hz), 2.71–2.59 (4 H, m), 2.12 (3 H, s); MS *m/e* (relative intensity) 160 (M^+, 1), 143 (2), 131 (1), 125 (1), 119 (1), 117 (5), 81 (3), 53 (9), 43 (100).

(*E*)-3-Chloro-3-octene-2,7-dione (5b): IR (film) 1715, 1688, 1618 cm^{-1}; UV_{max} (isopropyl alcohol) 238 nm (ε 10 980); NMR ($CDCl_3$) δ 6.96 (1 H, t with further fine splitting, J = 7 Hz), 2.74–2.56 (4 H, m), 2.39 (3 H, s), 2.17 (3 H, s); MS *m/e* (relative intensity) 176 (M^+, 1.5), 174 (M^+, 3.8), 139 (1.5), 138 (2), 133 (5), 131 (23), 95 (13), 67 (12), 53 (7), 43 (100).

(*E*)-2-Chloro-6-keto-2-heptenal Dimethyl Acetal (6). After a solution of 1.055 g (5.00 mmol) of 3-methoxy-3-methyl-2-oxa-7,7-dichloronorcarane (**2a**) in 7 mL of methanol was added to a stirred solution of 1.25 g (7.4 mmol) of silver nitrate in 18 mL of methanol, a white precipitate gradually formed. After 24 h, the reaction mixture was partitioned between brine and Et_2O. The organic phase was separated and dried ($MgSO_4$), and the solvent was removed in vacuo. Column chromatography afforded 915 mg (85%) of (*E*)-2-chloro-6-keto-2-heptenal dimethyl acetal (**6**) as a colorless oil: bp 90–95 °C (12 torr); IR (film) 1718, 1665 cm^{-1}; NMR ($CDCl_3$) δ 6.03 (1 H, t with further fine splitting, J = 7 Hz), 4.68 (1 H, s with fine splitting), 3.30 (6 H, s), 2.72–2.32 (4 H, m), 2.13 (3 H, s); spin decoupling by irradiation at 253 Hz (δ 2.53) collapsed the triplet at δ 6.03 to a singlet with fine splitting and the singlet at δ 4.68 sharpened but still exhibited fine splitting; MS *m/e* (relative intensity) 206 (M^+, 1), 177 (5), 176 (10), 175 (16), 174 (30), 133 (24), 131 (67), 97 (80), 75 (76), 53 (43), 43 (100).

Acknowledgments. The authors are grateful to Drs. W. Benz, D. Scheidl, and T. Williams, all of Hoffmann-La Roche Inc., Nutley, N.J., for the MS, microanalyses, and NMR spectra and the Charles and Johanna Busch Memorial Fund, the NIH (Biomedical Sciences Support Grant), and the Research Council, Rutgers University, for partial support of this work.

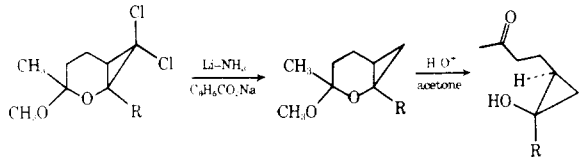
Registry No.—**1a,** 64331-96-0; **1b,** 64331-95-9; **2a,** 30823-17-7; **2b,** 55123-04-1; **3a,** 68200-81-7; **3b,** 68200-82-8; **4a,** 68200-76-0; **4b,** 68200-77-1; **5a,** 68200-78-2; **5b,** 68200-79-3; **6,** 68200-80-6.

References and Notes

(1) Part 8 in the series, "The Chemistry of 2-Alkoxy-3,4-dihydro-2*H*-pyrans". For part 7, see G. F. Weber and S. S. Hall, *J. Org. Chem.*, submitted for publication.
(2) Taken in part from the Ph.D. Thesis of G.F.W. that was submitted to the Graduate School, Rutgers University, Newark, N.J., May 1978.
(3) (a) M. Makosza and M. Wawrzyniewicz, *Tetrahedron Lett.*, 4659 (1969); (b) C. M. Starks, *J. Am. Chem. Soc.*, **93,** 195 (1971).
(4) S. S. Hall, G. F. Weber, and A. J. Duggan, *J. Org. Chem.*, **43,** 667 (1978).
(5) Dichloronorcarane **2a** is sufficiently labile that varying amounts of its rearrangement product (*E*)-2-chloro-6-keto-2-heptenal (**5a**) are also formed during the PTC-catalyzed reaction.
(6) A. J. Duggan and S. S. Hall, *J. Org. Chem.*, **40,** 2234 (1975).
(7) The formation of only one isomer seems to be unique for the 2-methyl substituted 2-methoxy-3,4-dihydro-2*H*-pyrans rather than for the carbene generation procedure since the same cis–trans mixture (27:73) was obtained from 2-methoxy-3,4-dihydro-2*H*-pyran with either PTC catalysis or with trichloroacetate and sodium methoxide.[6]
(8) As has been previously discussed in ref 6, the C-2 methoxy group should be axial in the preferential conformation of these 3,4-dihydro-2*H*-pyrans **1a** and **1b.**
(9) *cis*-2,2-Dichloro-3-(3-ketobutyl)-1-methylcyclopropanol (**3b**) is so labile

that its rearrangement product (*E*)-3-chloro-3-octene-2,7-dione (**5b**) is also isolated after acetylation.

(10) Since we have demonstrated [A. J. Duggan and S. S. Hall, *J. Org. Chem.*, **40**, 2238 (1975)] that the dichlorocarbene adducts can be reduced to 3-alkoxy-2-oxanorcaranes, this procedure constitutes a synthesis of the *cis*-3-(3-ketobutyl)cyclopropanols as well.



(11) L. Skattebøl, *J. Org. Chem.*, **31**, 1554 (1966).

(12) (a) E. B. Whipple, J. H. Goldstein, and G. R. McClure, *J. Am. Chem. Soc.*, **82**, 3811 (1960); (b) E. B. Whipple, J. H. Goldstein, and L. Mandell, *ibid.*, **82**, 3010 (1960).

(13) (a) R. C. DeSelms and U. T. Kreibich, *J. Am. Chem. Soc.*, **91**, 3659 (1969); (b) T. Ando, H. Yamanaka, and W. Funasaka, *Tetrahedron Lett.*, 2587 (1967); (c) L. Ghosez, P. Laroche, and G. Slinckx, *ibid.*, 2767 (1967); (d) W. F. Sliwinski, T. M. Su, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **94**, 133 (1972), and references cited therein; (e) D. B. Ledlie and W. H. Hearne, *Tetrahedron Lett.*, 4837 (1969).

(14) (a) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 395 (1965); (b) H. C. Longuet-Higgins and E. W. Abrahamson, *ibid.*, **87**, 2045 (1965); (c) P. v. R. Schleyer, W. F. Sliwinski, G. W. Van Dine, U. Schöllkopf, J. Paust, and K. Fellenberger, *ibid.*, **94**, 125 (1972), and references cited therein; (d) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry", Verlag Chemie, Weinheim/Bergstr., Germany, 1970, p 46; (e) C. H. DePuy, L. G. Schnack, J. W. Hausser, and W. Wiedemann, *J. Am. Chem. Soc.*, **87**, 4006 (1965).

(15) The IR spectra were determined with a Beckmann Model IR-9 infrared recording spectrophotometer. The UV spectra were determined with a Carey Model 14 ultraviolet recording spectrophotometer. The NMR spectra were determined at 100 MHz with a Varian Associates Model HA-100 NMR spectrometer, and decoupling was determined with a Varian Associates Model XL-100 NMR spectrometer. The chemical shifts are expressed in δ values (parts per million) relative to a Me_4Si internal standard. The mass spectra were obtained with a Consolidated Electronics Corp. Model 110-21B and a Varian Associates Model CH5 mass spectrometer. Gas chromatographic analyses (GLC) were performed on a Hewlett-Packard Model 402 high-efficiency chromatograph with a flame ionization detector attached to a Hewlett-Packard Model 3380A integrator.

(16) Data on **3a** (crude): IR (film) 3400 (br), 1717 cm^{-1}; NMR (60 MHz, $CDCl_3$) δ 4.00 (1 H, br s, exchanges in D_2O), 3.67 (1 H, d, J = 7.5 Hz), 2.87–2.57 (2 H, m), 2.10 (3 H, s), 2.00–1.37 (3 H, m).

(17) Data on **3b** (crude): IR (film) 3400 (br), 1715 cm^{-1}; NMR (60 MHz, CCl_4) δ 4.16 (1 H, br s, exchanges in D_2O), 2.63 (2 H, superficial t, J = ~7 Hz), 2.17 (3 H, s), 1.58 (3 H, s) superimposed on 2.0–1.4 (3 H, m).

Facile Product Isolation from Organostannane Reductions of Organic Halides

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The reduction of organic halides by organostannanes, first reported by vanderKerk et al.,[2] has subsequently found numerous applications. The reduction product has generally been separated from the organotin halide byproduct by distillation, gas chromatography, selective extraction, column chromatography, sublimation, a combination of some of these techniques, or in an unspecified manner.[3] We would like to report a facile, general method for the isolation of reduction products from the concomitantly formed organotin halide byproducts (eq 1).

$$\text{>C–X} + \text{>Sn–H} \rightarrow \text{>C–H} + \text{>Sn–X} \qquad (1)$$

In general, the reactants and products of the reduction reaction are all soluble in nonpolar organic solvents, and a simple solubility-based separation of the reduction product and the organotin halide cannot be achieved. In contrast to organotin chlorides, bromides, and iodides, trialkyl- and triaryltin fluorides are high melting, nonvolatile, insoluble (in both organic solvents and in water), "polymeric" materials.[4]

The desired separation of reduction product and organotin halide can be accomplished by conversion of the organotin halide (R_3SnX; X = Cl, Br, I) to the insoluble organotin fluoride by simply "extracting" the reduction mixture, dissolved in a nonpolar solvent, with a solution of potassium fluoride in water (eq 2). The original organotin halide is converted to an insoluble (in either the organic or aqueous phase) organotin fluoride which can be readily separated by filtration. The organic layer can be separated and dried and the solvent removed to yield the reduction product.[5]

$$R_3SnX + KF_{aq} \rightarrow R_3SnF\downarrow + KX_{aq} \qquad (2)$$

X = Cl, Br, I

As an example, the reduction of 1,3,5,7-tetrabromoadamantane to adamantane-*1,3,5,7-*d_4 in quantitative (crude) and 92% (isolated) yield is reported below. We suggest that this technique is of general utility and that it markedly facilitates product isolation in organostannane reductions.[6,7]

Experimental Section

Adamantane-*1,3,5,7-*d_4 (**1**) was prepared by the reaction (under nitrogen) of 9.5 g (0.021 mol) of 1,3,5,7-tetrabromoadamantane[8] with 25.0 g (0.086 mol) of tri-*n*-butyltin deuteride[9] in 100 mL of dry benzene at reflux for 24 h. After cooling, the benzene was removed on a rotary evaporator and the resultant residue was dissolved in 100 mL of ether. The ethereal solution was treated with excess KF in water (~10 g in 100 mL). The precipitated tri-*n*-butyltin fluoride was removed by filtration at reduced pressure, and the ether layer of the filtrate was separated and dried ($MgSO_4$). Removal of the solvent yielded 2.90 g (quantitative yield) of crude **1**; subsequent sublimation of the crude product yielded 2.70 g (92%) of **1**, mp 268–269 °C (sealed tube) [lit.[10] mp 269.6–270.8 °C (sealed tube)]. NMR and mass spectral analyses indicated ~95% d_4 incorporation.[11]

Acknowledgment. We thank the National Science Foundation for support of this work (Grant No. CHE77-07808).

Registry No.—**1**, 19215-02-2; 1,3,5,7-tetrabromoadamantane, 7314-86-5; tri-*n*-butyltin deuteride, 6180-99-0; tri-*n*-butyltin fluoride, 1983-10-4.

Supplementary Material Available: A complete list of references to organotin hydride reductions of alkyl halides to late 1977 (3 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Address correspondence to this author at Tulane University.

(2) G. J. M. vanderKerk, J. G. Noltes, and J. G. A. Luitjen, *J. Appl. Chem.*, **7**, 366 (1957).

(3) A complete list of references (ca. 125) is not presented here but is available as supplementary material. See paragraph at the end of paper about supplementary material.

(4) The tin atoms in solid trialkyltin fluorides are pentacoordinate: e.g., the crystal structure of $(CH_3)_3SnF$ consists of planar $(CH_3)_3Sn$ units linked by interspersed (nonequivalent) fluorines $[\cdots(CH_3)_3Sn\cdots F\cdots(CH_3)_3Sn\cdots F)_n\cdots]$: H. C. Clark, R. J. O'Brien, and J. Trotter, *Proc. Chem. Soc., London*, 85 (1963); *J. Chem. Soc.*, 2332 (1964); K. Yasuda, Y. Kawasaki, N. Kasai, and T. Tanaka, *Bull. Chem. Soc. Jpn.*, **38**, 1216 (1965). Similarly, solid dimethyltin difluoride exists as an infinite two-dimensional array of pentacoordinate Sn atoms: E. O. Schlemper and W. C. Hamilton, *Inorg. Chem.*, **5**, 995 (1966).

(5) Organotin halide impurities occurring in preparations of tetraalkyl and tetraaryl organotin compounds have been removed by a similar procedure; see W. P. Neumann, "The Organic Chemistry of Tin", Interscience, New York, 1970, pp 23 and 49.

(6) A similar reaction in which the product was sublimed directly from the reaction mixture yielded only 34% of the theoretical amount of product. It should be noted that substantially higher yields have been reported in similar reactions; e.g., adamantane-d_1 has been isolated in ~90% yield from the reduction of adamantyl bromide with tri-*n*-butyltin deuteride by a sublimation procedure: E. W. Della and H. K. Patney, *Synthesis*, 251 (1976).

(7) An alternate procedure for the reduction of alkyl halides employing lithium aluminum hydride and catalytic amounts of organotin halides has been reported [H. G. Kuivila, *Adv. Organomet. Chem.*, **1**, 47 (1964)], but this modification has not found general use.

(8) H. Stetter and C. Wulff, *Chem. Ber.*, **93**, 1366 (1960).

(9) Alfa Inorganics, Inc., product employed without further purification.

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